Synthesis of 1,4-bis(1,3,4-oxadiazol-2-yl)-2,5-dialkoxybenzene–oligothiophene copolymers with different emissive colors: synthetically tuning the photoluminescence of conjugated polymers

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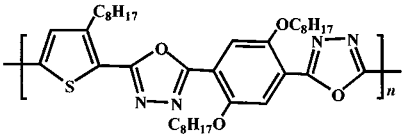
The copolymers of oligothiophenes and 1,4-bis(1,3,4-oxadiazol-2-yl)-2,5-dialkoxybenzene were synthesized with blue, green and orange emissive light depending on the length of the oligothiophene.

In the past few years, π-conjugated polymers have been intensively studied for applications in polymer light-emitting diodes (PLEDs).[1–3] One of the significant advantages of polymer electroluminescent materials is the ease with which the emissive wavelength can be tuned, especially for the realization of blue light.[1] The emissive spectrum of a conjugated polymer basically depends on its π–π^* band gap, which can be tailored using different backbone structures.[1,2] For polymers with the same backbone structure, the emissive spectra could also be tuned by attaching different functional groups or/and by controlling the steric conformation of the backbone through synthetic methodology.[4,5] Another effective approach to tuning emissive color is to block the extension of conjugation by inserting non-conjugated groups or other conjugation-blocking groups into the backbone of a conjugated polymer.[6–10] For the conjugation-interrupted approach, thiophene-based polymers have attracted special attention because of the environmental stability of polythiophenes and the ease of synthesis and modification of oligothiophenes. It has been proven that oligothiophenes with different numbers of thiophene rings can emit from blue to red fluorescence.[11] We present here a new synthetic approach to tune the emissive spectra of totally conjugated polymers based on oligothiophenes.

Our new approach incorporates two types of conjugated blocks together to construct a conjugated polymer backbone. One of the two conjugated blocks has a small band gap, while the other has a relatively large band gap. With the fact that head-to-tail regioregular poly(3-alkylthiophenes) may emit light with λ_{max} at around 725 nm,[12] oligomers of 3-alkylthiophene can therefore be used as the smaller band gap blocks in our design. On the other hand, most 1,3,4-oxadiazole-containing conjugated polymers and molecular materials exhibit quite large band gaps (larger than 3.0 eV).[13] Therefore 1,4-bis(1,3,4-oxadiazol-2-yl)benzene was chosen as the larger band gap block in the newly designed polymers **1**–**3**. These polymers may be seen as polythiophene-based polymers, in which the 1,4-bis(1,3,4-oxadiazol-2-yl)benzene group is inserted into the backbone. The extension of conjugation along the backbone of polythiophene is limited or changed, but not interrupted, due to the existence of the 1,4-bis(1,3,4-oxadiazol-2-yl)benzene groups. The conjugated length of the oligothiophenes can be controlled and different functional groups can be attached to the thiophene ring and the benzene ring in the 1,4-bis(1,3,4-oxadiazol-2-yl)benzene moiety, which will result in variation of the emission spectra of the resultant polymers and enhance the solubility of the polymers.

The general synthetic procedure for polymers **1**–**3** is displayed in Scheme 1. The dicarbonyl chlorides **4**–**6** were prepared from the corresponding monomer, dimer and trimer of 3-alkylthiophene, which were synthesized as described in the literature,[14,15] by carboxylation at the α-positions of the thiophene rings with Bu^nLi and dry ice and subsequent reaction with $SOCl_2$.[15] The dihydrazide **7** was prepared from diethyl 2,5-dioctyloxyterephthalate, which was obtained from diethyl 2,5-dihydroxyterephthalate *via* reaction with 1-bromooctane, through a reaction with excess hydrazine monohydrate. The chemical structures and purity of all the compounds were identified by ^1H and ^{13}C NMR, mass and elemental analyses. The polycondensation between the dicarbonyl chlorides and the dihydrazide in *N*-methylpyrrolidinone (NMP) in the presence of LiCl and pyridine afforded the polyhydrazides **1′**–**3′**. The polyhydrazides were isolated by pouring the reaction mixtures into water and then filtering and washing with water and EtOH. The polyhydrazides were converted to the final polymers **1**–**3** by refluxing in $POCl_3$. Pouring the reaction mixtures into water



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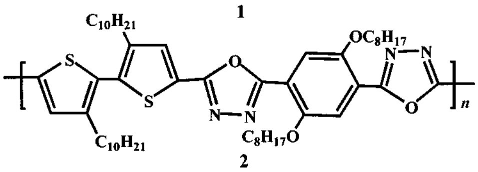

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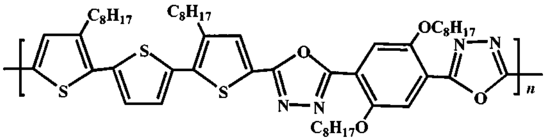

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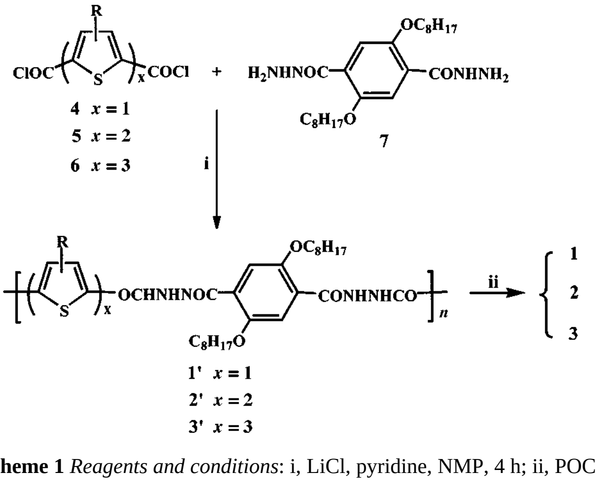

Scheme 1 *Reagents and conditions*: i, LiCl, pyridine, NMP, 4 h; ii, $POCl_3$, reflux, 6 h

precipitated the final polymers. Polymers **1–3** were obtained as gray, yellow and orange powders, respectively, after being washed with water, EtOH and Et_2O and dried under reduced pressure at room temperature. Polymers **1** and **3** are partially soluble in both $CHCl_3$ and THF. Polymer **2** is completely soluble in $CHCl_3$ and partially soluble in THF. However, all the three polymers readily dissolve in a mixture of $CHCl_3$ with a small amount of TFA to give clear solutions. By means of gel permeation chromatography (GPC) using THF as eluent and polystyrene as standard, the molecular weights of the THF soluble parts of the polymers were measured to be M_n = 5419 (M_w/M_n = 1.9) for polymer **1**, 7574 (2.0) for polymer **2**, and 2814 (1.4) for polymer **3**. The actual molecular weights of the polymers should be much higher than these measured values because of the insolubility of the parts with higher molecular weights. The structures of the polymers were confirmed by ^1H and ^{13}C NMR and elemental analyses.‡

The absorption and fluorescence spectra of polymers **1–3** as films are shown in Fig. 1. The films were prepared *via* spin-coating on a quartz plate using solutions of the polymers in $CHCl_3$ with a small amount of TFA. The expected gradual bathochromic shift of the absorption spectra is exhibited with the increasing length of oligothiophenes in the polymers. The absorption maximum increases from **1** (λ_{max} = 420 nm) to **2** (λ_{max} = 441 nm) to **3** (λ_{max} = 461 nm). The absorption spectra of all the three polymers are structured, as indicated by the well-defined sub-peaks or shoulders at 360 and 443 nm for **1**, 419 and 471 nm for **2**, and 439 and 494 nm for **3**. It is worth noting that the structures in the spectra become less defined on going from **1** to **3**. This phenomenon implies that the polymers with shorter oligothiophenes have a more regular structure in the solid state. Polymers **1–3** in the solid state emit intense blue, green and orange light, respectively, upon UV–VIS excitation (λ > 350 nm). The peak wavelengths in the emission are 489 nm for **1**, 530 nm for **2**, and 579 nm for **3,** respectively. The emissive spectra are much less structured than the absorption spectra. The Stokes shifts were determined to be 69 nm for **1**, 89 nm for **2**, and 118 nm for **3**. The spectral difference among the three polymers could be further ascribed to differences in the internal charge transfer along the backbones of the polymers in their excited states.

Comparing the spectral data with those of alkyl-substituted oligothiophenes and conjugation-interrupted polymers based on oligothiophenes,[8–10, 16–18] polymers **1–3** correspond to the effective conjugated length of about three, four to five, and five to six extended thiophene rings, respectively. It is evident that the 1,4-bis(1,3,4-oxadiazol-2-yl)benzene moiety does not play a role as a conjugation-interrupting block in the polymers, but is a part of the whole conjugated structure. Its contribution to conjugation is equivalent to about two to three extended thiophene rings.

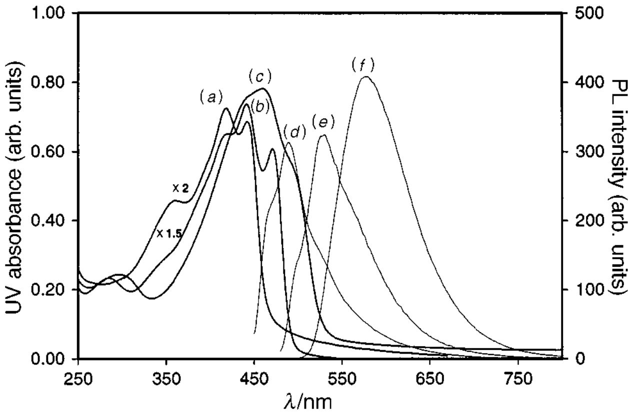

Fig. 1 Absorption [(*a*) 1, (*b*) **2** and (*c*) **3**]and fluorescence [(*d*) **1**, (*e*) **2** and (*f*) **3**] spectra of polymers **1–3** in films at room temperature

In conclusion, we have synthesized a new series of totally conjugated copolymers consisting of oligothiophenes and 1,4-bis(1,3,4-oxadiazol-2-yl)-2,5-dioctyloxybenzene. The emissive color of the copolymers could be tuned from blue to green to orange by increasing the number of thiophene ring in the oligothiophene blocks from one to three. The 1,4-bis(1,3,4-oxadiazol-2-yl)-2,5-dioctyloxybenzene block acts as part of the whole conjugated structure and is equivalent to about two to three thiophene rings. Another important aspect of this contribution to electroluminescent polymeric materials is that it might provide an effective approach to the synthesis of n-doped type electroluminescent materials with different emissive colors due to the high electron affinity of 1,3,4-oxadiazole.

Notes and References

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‡ *Selected data* for Polymer **1**: δ_H($CDCl_3$–CF_3CO_2D, 20:1) 7.93 (s, 1H), 7.74 (d, 2H), 4.23 (s, 4H), 3.20 (t, 2H), 2.00–1.60 (br, 6H), 1.60–1.15 (br, 30H), 0.83 (m, 9H) (Calc. for $C_{38}H_{54}N_4SO_4$: C, 68.85; H, 8.21; N, 8.46; S, 4.84. Found: C, 68.01; H, 8.20; N, 8.94; S, 4.33%). For Polymer **2**: δ_H($CDCl_3$) 7.84 (s, 2H), 7.75 (s, 2H), 4.19 (t, 4H), 2.62 (t, 4H), 1.93 (br, 4H), 1.59 (br, 8H), 1.23 (br, 44H), 0.84 (t, 12); δ_C($CDCl_3$) 162.71, 160.99, 150.84, 144.39, 132.19, 131.09, 125.30, 116.36, 114.57, 69.65, 31.78, 30.50, 29.52, 29.48, 29.30, 29.23, 28.88, 26.05, 22.56, 13.99 (Calc. for $C_{54}H_{80}N_4S_2O_4$: C, 71.01; H, 8.83; N, 6.13; S, 7.02. Found: C, 70.46; H, 9.14; N, 6.11; S, 7.13%). For Polymer **3**: δ_H($CDCl_3$–CF_3CO_2D, 20:1) 7.92 (s, 2H), 7.76 (s, 2H), 7.38 (s, 2H), 4.28 (t, 4H), 2.94 (br, 4H), 1.97 (br, 4H), 1.78 (br, 4H), 1.65–1.00 (br, 34H), 0.87 (br, 12 H); δ_C($CDCl_3$) 162.42, 160.92, 150.84, 140.86, 135.82, 135.14, 132.38, 127.20, 122.49, 116.40, 114.56, 69.72, 31.79, 30.37, 29.60, 29.38, 29.21, 26.11, 22.58, 14.00 (Calc. for $C_{54}H_{74}N_4S_3O_4$: C, 69.04; H, 7.94; N, 5.96; S, 10.24. Found: C, 67.54; H, 8.83; N, 6.08; S, 10.29%).

1 N. C. Greenham and R. H. Friend, in *Solid State Physics*, ed. H. Ehrenreich and F. Spaepen, Academic Press, London, 1995, vol. 49, p. 2.
2 F. Hide, M. A. Díaz-García, B. J. Schwartz and A. J. Heeger, *Acc. Chem. Res.*, 1997, **30**, 430.
3 A. Kraft, A. C. Grimsdale and A. B. Holmes, *Angew. Chem., Int. Ed.*, 1998, **37**, 402.
4 B. Xu and S. Holdcroft, *Macromolecules*, 1993, **26**, 4457.
5 M. Berggren, O. Inganäs, G. Gustafsson, J. Rasmusson, M. R. Anderson, T. Hjeertberg and O. Wennerström, *Nature*, 1994, **372**, 444; M. R. Anderson, M. Berggren, O. Inganäs, G. Gustafsson, J. C. Gustafsson-Carlberg, D. Selse, T. Hjeertberg and O. Wennerström, *Macromolecules*, 1995, **28**, 7525.
6 B. L. Burn, A. B. Holmes, A. Kraft, D. D. C. Bradley, A. R. Brown, R. H. Friend and R. W. Gymer, *Nature*, 1992, **356**, 47.
7 M. Hay and F. L. Klavetter, *J. Am. Chem. Soc.*, 1995, **117**, 7112.
8 W. Li, T. Maddux and L. Yu, *Macromolecules*, 1996, **29**, 7329.
9 B. S. Kang, M.-L. Seo, Y. S. Jun, C. K. Lee and S. C. Shin, *Chem. Commun.*, 1996, 1167.
10 Y. Kunugi, L. L. Miller, T. Maki and A. Canavesi, *Chem. Mater.*, 1997, **9**, 1061.
11 D. Fichou, M.-P. Teulade-Fichou, G. Horowitz and F. Demanze, *Adv. Mater.*, 1997, **9**, 75.
12 K. A. Murray, S. C. Moratti, D. R. Baigent, N. C. Greenham, K. Pichler, A. B. Holmes and R. H. Friend, *Synth. Met.*, 1995, **69**, 395.
13 X.-C. Li, A. Kraft, R. Cervini, G. C. W. Spencer, F. Cacialli, R. H. Friend, J. Gruener, A. B. Holmes, J. C. De Mello and S. C. Moratti, *Mater. Res. Soc. Symp. Proc.*, 1996, **413**, 13**.**
14 R. D. McCullough, R. D. Lowe, M. Jayaraman and D. L. Anderson, *J. Org. Chem.*, 1993, **58**, 904.
15 W.-L. Yu, H. Meng, J. Pei, W. Huang, Y. F. Li and A. J. Heeger, *Macromolecules*, 1998, **31**, 4838.
16 A. Yassar, D. Delabouglise, M. Hmyene, B. Nessak, G. Horowitz and F. Garnier, *Adv. Mater.*, 1992, **4**, 490.
17 R. A. J. Janssen, L. Smilowitz, N. S. Sariciftci and D. Doses, *J. Chem. Phys.*, 1994, **101**, 1787.
18 P. F. van Hutten, R. E. Gill, J. K. Herrema and G. Hadziioannou, *J. Phys. Chem.*, 1995, **99**, 3218.

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